

# Synthesis of Bimetallic AuPt Clusters with Clean Surfaces via Sequential Displacement-Reduction Processes

Alexandra M. Landry and Enrique Iglesia\*

Department of Chemical Engineering, University of California, Berkeley, California 94720, United States Chemical Sciences Division, E.O. Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

## **Supporting Information**

**ABSTRACT:** We report the synthesis of bimetallic AuPt nanoparticles (3.3-4.3 nm) of uniform size and composition using colloidal methods and reagents containing only C, H, O, and N. These clusters were dispersed onto SiO<sub>2</sub> and treated at low temperatures in the presence of reductants to remove all surface residues without concomitant agglomeration, thus leading to bimetallic structures suitable for mechanistic inquiries into bimetallic effects on surface reactivity. Synthesis protocols exploit and generalize galvanic displacement-reduction (GDR) processes previously used to prepare AuPd clusters; these routes promote bimetallic mixing but become more challenging for systems (e.g., AuPt) with smaller reduction potential differences and less favorable mixing enthalpies than AuPd. These hurdles are addressed here through proce-



dural modifications that inhibit the formation of large Au-rich clusters, which compromise size and compositional uniformity. In doing so, we extend GDR techniques to endothermic alloys with elements of more similar redox properties. Higher temperatures and lower Au<sup>3+</sup> precursor concentrations promoted metal mixing and inhibited homogeneous and heterogeneous nucleation. Cluster size and compositional uniformity were confirmed by UV–visible spectroscopy during and after colloid formation, transmission electron microscopy, and high-angle annular dark-field (HAADF) imaging with energy-dispersive X-ray spectroscopy (EDS). Particle-by-particle EDS analysis and HAADF imaging demonstrated the prevalence of GDR processes in AuPd bimetallic cluster assembly. These methods also showed that size-dependent intracluster diffusion during AuPt cluster formation, driven by unfavorable AuPt mixing thermodynamics, leads to Au surface enrichment, thus promoting autocatalytic Au deposition. This rigorous mechanistic comparison of AuPt and AuPd systems provides essential guidance and specific control variables and procedures for the synthesis of other bimetallic systems based on the redox potential differences and mixing thermodynamics of their two components.

# 1. INTRODUCTION

The combination of two metals within a small crystallite of nanometer dimensions can lead to marked consequences for turnover rates and selectivities in the practice of heterogeneous catalysis.<sup>1,2</sup> Bimetallic catalysts are known to increase rates and improve selectivity of Fischer–Tropsch synthesis;<sup>3</sup> they are also used for NO<sub>x</sub> reduction and CO oxidation reactions,<sup>4,5</sup> as well as in electrodes for methanol and H<sub>2</sub> fuel cells.<sup>6</sup> The development of rigorous mechanistic descriptions of the effects of atomic metal mixing and their applications in predictive catalyst design criteria require the preparation of bimetallic clusters that are uniform in both size and chemical composition, but which also expose surfaces free of residual synthetic detritus. Conventional catalyst synthesis protocols, such as incipient wetness impregnation, seldom deposit the two metals within the same cluster, thus failing to provide the intimate metal mixing required for bimetallic synergies.<sup>7</sup> Also, the broad particle size distributions typical of such techniques convolute the consequences of bimetallic mixing and cluster size.<sup>8</sup>

Colloidal synthesis methods, in contrast, provide greater control of the final particle size and composition<sup>2,11</sup> but typically require reagents containing heteroatoms (e.g., S or B) that block active structures at catalyst surfaces. Nonuniformity in cluster composition and size, together with these ubiquitous surface impurities, have frequently led to ambiguous and imprecise interpretations of bimetallic effects in catalysis.

Our recent studies have provided evidence for sequential galvanic displacement-reduction (GDR) processes in the formation of AuPd clusters.<sup>12</sup> These synthetic protocols use weakly coordinating reagents containing only C, H, O, and N atoms and form clusters uniform in size and composition. Reagents can be readily removed, without marked consequences for the size or composition of clusters, using oxidants such as  $O_{3}$ ,<sup>12</sup> in some cases with ultraviolet irradiation,<sup>13</sup> or by carrying out

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<sup>a</sup>Surface atoms of seed particles composed of  $M_A$  reduce  $M_B$  cations due to a positive  $\Delta E^o_{redox}$  and are concurrently oxidized into solution (step 2a). The reductant (ethanol or ethylene glycol) subsequently rereduces the oxidized seed surface atoms back onto growing bimetallic particle surfaces (step 2b). Heterogeneous or homogeneous nucleation of Au (step 1) must be avoided to ensure size and compositional uniformity.

treatments at low temperatures in reducing environments, as the current study demonstrates. GDR synthesis protocols start with colloidal suspensions of preformed seed clusters of the element  $(M_A)$  with the lower standard reduction potential  $(E^{\circ})$ ; these suspensions are then mixed with a solution of metal precursors of the second element  $(M_B; Scheme 1)$ . The surface metal atoms in the seed clusters reduce the metal precursors in solution, driven by the favorable thermodynamics inherent in the positive  $\Delta E^{\circ}_{
m redox}$ values  $(\Delta E_{\text{redox}}^{\circ} = E_{\text{red. (MA)}}^{\circ} - E_{\text{ox. (MB)}}^{\circ} > 0)$  for the overall redox reaction (Scheme 1,2a). Such reactions lead to the deposition of the second metal onto the MA seed clusters, while surface atoms of the seed clusters are oxidized and brought into solution as solvated cations. Solvent molecules are present at much greater concentrations than the counterions of the M<sub>A</sub> precursors (e.g.,  $Cl^{-}$  or  $NO_{3}^{-}$ ), thus ensuring that displaced  $M_{A}$  cations (e.g., Pt or Pd) are coordinated by the solvent and subsequently reduced by the solvent, also acting as a reductant, back onto growing bimetallic cluster surfaces (Scheme 1.2b) at faster rates than the reduction of  $M_B$  metal cations with coordinating counterions (e.g., HAuCl<sub>4</sub>).<sup>14</sup> Galvanic displacement (Scheme 1,2a) is therefore the sole kinetically relevant step for the GDR reduction route.12

These GDR steps were previously shown to form AuPd nanoparticles starting from Pd seed clusters.<sup>12</sup> The mechanistic details of such synthesis protocols led us to infer that similar approaches would succeed for other bimetallic combinations, provided that the suspensions initially contained clusters of the element with the lower standard reduction potential (Table 1).

 
 Table 1. Standard Reduction Potentials of Metals of Catalytic Interest<sup>15</sup>

element	$E^{\circ}$ = standard reduction potential (V)
Au <sup>3+</sup>	1.52
Pt <sup>2+</sup>	1.18
Pd <sup>2+</sup>	0.99
lr <sup>3+</sup>	0.92
Ag <sup>1+</sup>	0.80
Rh <sup>2+</sup>	0.60
Ru <sup>3+</sup>	0.38
Ni <sup>2+</sup>	-0.26
Co <sup>2+</sup>	-0.28

We show here that, with minor modifications in synthesis protocol, this is the case for AuPt particles formed from Pt seed particles; we also confirm the relevant mechanistic details for both AuPt and AuPd systems by means of rigorous statistical analysis of the size and composition of individual bimetallic clusters using electron microscopy. Specifically, we use energydispersive X-ray spectroscopy (EDS) and high-angle annular dark-field (HAADF) imaging to determine the size and composition of a large number (>100) of AuPd and AuPt clusters (<5.5 nm) prepared using these methods. The small size of such clusters is essential for their function as catalysts but requires state-of-the-art methods to accurately assess the composition of each particle, thus requiring the sensitivity of the advanced EDS detectors used here.

The data obtained and reported here confirm that Pd seed clusters act as reductants during bimetallic formation; the rate of Au<sup>3+</sup> reduction (and of Pd<sup>0</sup> oxidation) is proportional to the seed cluster surface area for AuPd.<sup>12</sup> This is in contrast to AuPt, for which the larger seeds consume more Au than expected from their surface areas alone. Unlike Au-Pd, Au and Pt atoms mix endothermically ( $\Delta H_{AuPt} = +2.3 \text{ kJ mol}^{-1}$  vs  $\Delta H_{AuPd} = -6.7 \text{ kJ mol}^{-1}$ ),<sup>16,17</sup> thus driving metal atoms to segregate within clusters by placing the metal with the lower surface energy (Au)<sup>18</sup> preferentially at cluster surfaces.<sup>19,20</sup> Larger clusters with larger bulk reservoirs of Au maintain the thermodynamic driving force for Au surface enrichment by mitigating the depletion of Au from the bulk upon segregation, consequently increasing their Au<sup>0</sup> surface contents.<sup>21</sup> The Au-rich cluster surfaces of the larger AuPt clusters impede GDR reduction routes by minimizing accessible Pt<sup>0</sup> atoms and instead promoting the fast autocatalytic reduction of Au cations on Au<sup>0</sup> atoms,<sup>22,23</sup> thus scavenging solvated Au cations and preventing their ultimate deposition onto smaller clusters.

The smaller  $\Delta E^{\circ}_{redox}$  driving force for displacement reactions (Scheme 1,2a), the stronger (competing) reductant required as the solvent (ethylene glycol for AuPt vs ethanol for AuPd; Scheme 1,1), and the enrichment of bimetallic surfaces with Au<sup>0</sup> impose additional hurdles in the synthesis of uniform AuPt clusters relative to AuPd clusters. As a result, more precise protocols become essential to avoid the enrichment of the larger Pt seed clusters with Au and the homogeneous or heterogeneous nucleation of Au-rich clusters (illustrated in Scheme 1,1), both of which detract from the size and compositional uniformity that we seek in these materials. In the synthetic protocols that we report here, the continuous addition of low concentrations of solvated Au precursors is used to inhibit Au nucleation, while higher synthesis temperatures are used to compensate for the unfavorable mixing enthalpies through mixing entropies that become more consequential for Gibbs free energies as temperature increases.

#### 2. EXPERIMENTAL SECTION

**2.1.** Synthesis of Monometallic and Bimetallic Nanoparticles. 2.1.1. Monometallic Pd Clusters Protected by Poly(vinyl alcohol) (PVA). The synthesis of the parent Pd clusters has been described elsewhere.<sup>12</sup> Briefly, Pd(NO<sub>3</sub>)<sub>2</sub>·2(H<sub>2</sub>O) (5 × 10<sup>-4</sup> M, Sigma-Aldrich, ~ 40% Pd basis) was dissolved in a solution of 1:1 by volume ethanol (EtOH, Sigma-Aldrich, >99.5%) and deionized water (H<sub>2</sub>O; resistivity ~0.06  $\mu$ S cm<sup>-1</sup>) containing PVA (0.02 M PVA, monomeric unit basis; 31 000–51 000 amu, Sigma-Aldrich). The solution was

Scheme 2. Colloidal Synthesis Protocols via Sequential Galvanic Displacement-Reduction Processes<sup>a</sup>



<sup>*a*</sup>(a) Metal precursor  $M_A$  (big dark circle) and the protecting polymer (squiggly line) are combined in a reductive solvent (small black dot) and heated to form a suspension of polymer-protected seed clusters; (b) metal precursor  $M_B$  (big light circle) is added to the suspension and (c) subsequently reduced and incorporated into the monometallic seed clusters to form bimetallic clusters; (d) clusters are dispersed onto a support and (e) the polymer is removed before catalytic studies.

treated at 368 K (Scheme 2a) for 0.5 h, which led to a color change from yellow to black, indicative of the reduction of the metal precursors and the formation of metal clusters. UV–visible spectra of the suspension did not show any residual features of the Pd complexes, confirming their complete reduction.

2.1.2. Monometallic Pt Clusters Protected by Polyvinylpyrrolidone (PVP).  $H_2PtCl_6$  (Sigma-Aldrich, 8% wt. in  $H_2O$ ) was dissolved in a solution of ethylene glycol (EG, Fischer Scientific) containing PVP (0.02 M, monomeric unit basis; 40 000 amu, Sigma-Aldrich). Heating the solution in ambient air at 423 K (Scheme 2a) for 0.5 h led to a color change from yellow to brown, indicative of the reduction of the metal precursors and the formation of metal clusters. UV–visible spectra of the suspension did not show any residual features of the Pt complexes, confirming their complete reduction.

EG, and not the EtOH/ $H_2O$  mixtures used to synthesize Pd clusters (Section 2.1.1), was required to stabilize Pt seed clusters. Pt clusters synthesized in EtOH/ $H_2O$  (with PVP or PVA) flocculated, forming large aggregates visible as precipitates and as deposits on glass surfaces of containers.

2.1.3. Monometallic Au Clusters Protected by PVP. HAuCl<sub>4</sub>·  $3(H_2O)$  (5 × 10<sup>-4</sup> M, Sigma-Aldrich) was dissolved in a solution of EG (Fischer Scientific) containing PVP (0.02 M, monomeric unit basis; 40 000 amu, Sigma-Aldrich). Treating the solution at 423 K (Scheme 2a) for 0.5 h led to a color change from yellow to red, indicative of the reduction of the metal precursors and the formation of metal clusters.

2.1.4. AuPd Clusters Protected by PVA. The procedures used for the synthesis of AuPd clusters have been described elsewhere.<sup>12</sup> Briefly, a solution of HAuCl<sub>4</sub>·3(H<sub>2</sub>O) ( $5 \times 10^{-4}$  M, Sigma-Aldrich) dissolved in 1:1 by volume EtOH (Sigma-Aldrich, >99.5%) and deionized H<sub>2</sub>O (resistivity ~0.06  $\mu$ S cm<sup>-1</sup>) was added to a suspension of monometallic Pd clusters ( $5 \times 10^{-4}$  M, Pd atom basis; prepared as described in Section 2.1.1) and allowed to stir (310 rpm) for 2 h at ambient temperature in air (Scheme 2b). UV–visible spectra of the suspensions did not show any residual features of the Au complexes, confirming their complete reduction. Equal volumes of the Au precursor solution and Pd seed cluster suspension were combined to form Au<sub>50</sub>Pd<sub>50</sub> clusters. Other compositions were prepared by changing the volumetric ratio of the Au precursor solution and Pd seed cluster suspension.

2.1.5. AuPt Clusters Protected by PVP. A Pt cluster suspension  $(5 \times 10^{-4} \text{ M}, \text{Pt} \text{ atom basis}; \text{ prepared as described in Section 2.1.2}) was heated while stirring (310 rpm) for 0.17 h in a two-neck round-bottom flask placed within an oil bath held at 423 K. A solution of HAuCl<sub>4</sub>·3(H<sub>2</sub>O) (5 × 10<sup>-4</sup> M, Sigma-Aldrich) in EG was added at 16.7 nmol Au<sup>3+</sup> s<sup>-1</sup> using a syringe pump (KD Scientific KDS 100); the resulting mixture was allowed to stir (310 rpm) for 0.5 h at 423 K in air with a reflux condenser. UV–visible spectra of the suspensions did not show any residual features of the Au precursor solution and the Pt seed cluster suspension were combined to form Au<sub>50</sub>Pt<sub>50</sub> clusters. Other compositions were prepared by changing the volumetric ratio of the Au precursor solution and Pt seed cluster suspension.$ 

**2.2. Elemental Analysis of Bimetallic Clusters.** High-angle annular dark-field (HAADF) imaging and energy-dispersive X-ray spectroscopy (EDS) were used to determine the diameter and composition, respectively, of individual bimetallic nanoparticles. EDS measurements were obtained using an FEI Titan microscope

operated at 200 kV and equipped with an FEI Super X-Quad windowless detector based on silicon drift technology. EDS data were analyzed using Bruker Esprit software calibrated against mineral standards for quantitative accuracy and with Cliff-Lorimer k-factors for quantification. Scanning transmission electron microscopy (STEM) images were acquired using a HAADF detector with a convergence semiangle ( $\alpha$ ) of 10 milliradians and an inner semiangle ( $\beta$ ) of 50 milliradians. Cluster diameters were obtained from HAADF images using ImageJ software. Over 100 individual particles were analyzed for each bimetallic sample (Au<sub>33</sub>M<sub>A,67</sub>, Au<sub>50</sub>M<sub>A,50</sub>, Au<sub>67</sub>M<sub>A,33</sub>; M<sub>A</sub> = Pt or Pd). The volume-weighted mean atomic fraction ( $\langle X_M \rangle_{at.}$ ) of metal M (Au, Pt, or Pd) within a bimetallic sample was calculated using the equation:

$$\langle X_{\rm M} \rangle_{\rm at.} = \frac{\sum X_{{\rm M}_i i} d_i^3}{\sum d_i^3} \tag{1}$$

where  $X_{M,i}$  is the atomic fraction of metal M in particle *i* and  $d_i$  is the diameter. Eq 1 accounts for the greater atomic contribution of the larger particles to the total metal content.

Samples were prepared for microscopy by placing a drop of a suspension containing the clusters onto holey-carbon Cu grids (Ted Pella Inc.). AuPd samples were deposited directly from their EtOH/ $H_2O$  synthesis media, which evaporated at ambient temperature. AuPt nanoparticles suspended in EG were first redispersed in a more volatile solvent, EtOH (Sigma-Aldrich, >99.5%), by adding acetone (10 cm<sup>3</sup>, Fisher Scientific) to a suspension of AuPt clusters in EG (2 cm<sup>3</sup>) to flocculate the clusters, collecting precipitates by centrifugation (133 Hz, 0.6 ks), and redispersing clusters in 1 cm<sup>3</sup> of EtOH. The solvent was then removed by evaporation in ambient air without thermal treatments that could affect cluster size and composition.

**2.3. Ultraviolet–Visible Spectroscopy.** Ultraviolet–visible (UV–visible) spectra of cluster suspensions were measured using quartz cuvettes (10 cm<sup>3</sup>, Agilent) and a two-beam spectrophotometer (Varian Cary 400 Bio). Spectra were collected in the 200–800 nm spectral range at scan rates of 5 nm s<sup>-1</sup>. Time-dependent spectra obtained during the synthesis reaction were measured by quenching the synthesis mixture using an ice bath at designated time intervals and collecting spectra of the dispersions at ambient temperature. The intensities of the ligand-to-metal charge transfer (LMCT) band of HAuCl<sub>4</sub> (323 nm) and of the localized surface plasmon resonance (LSPR) band of Au-covered surfaces (530 nm) were used to monitor the reduction of Au<sup>3+</sup> (to Au<sup>+</sup> or Au<sup>0</sup>) and the nucleation of Au particles, respectively. The absorbance in a spectral range free of detectable features, the background (410 nm), was used to monitor the total mass of suspended particles.

The LMCT and LSPR bands were deconvoluted for more accurate analysis using previously reported procedures.<sup>12</sup> The spectra were first regressed to an exponential function excluding the LMCT (300–500 nm) and/or LSPR (400–650 nm) spectral regions. The regressed background curve was subtracted from the spectra, and the intensity of the LMCT or LSPR bands was used to determine qualitative amounts of Au<sup>3+</sup> in solution or Au<sup>0</sup> at cluster surfaces, respectively.<sup>12</sup>

**2.4.** Dispersion of Polymer-Protected Particles onto SiO<sub>2</sub>. Clusters were dispersed onto fumed SiO<sub>2</sub> (0.51 g; Sigma-Aldrich, 7 nm particle size, 395 m<sup>2</sup> g<sup>-1</sup> surface) by suspending SiO<sub>2</sub> in deionized water (0.052 L, resistivity ~0.06  $\mu$ S cm<sup>-1</sup>) and adding the colloidal suspension dropwise (0.052 L, ~0.2 cm<sup>3</sup> s<sup>-1</sup>). The mixed slurry was stirred (310 rpm) at ambient temperature for 1 h, and the solids were



Figure 1. Particle size distributions and sample transmission electron micrographs for (a) Pt clusters and bimetallic (b)  $Au_{33}Pt_{67}$ , (c)  $Au_{50}Pt_{50}$ , and (d)  $Au_{67}Pt_{33}$  clusters.

recovered by centrifugation (133 Hz, 0.6 ks; Scheme 2d). The complete dispersion of all clusters on the silica support was confirmed by the absence of any background intensity in the UV–visible spectra of the supernatant solutions. The SiO<sub>2</sub>-supported clusters were stirred (310 rpm) in deionized water (0.052 L, resistivity ~0.06  $\mu$ S cm<sup>-1</sup>) for 1 h and collected by centrifugation two more times before treating samples overnight at 356 K in ambient air. These procedures led to metal loadings of 1% wt.

**2.5. Transmission Electron Microscopy (TEM).** Bright-field transmission electron micrographs were obtained using a JEOL 1200 EX microscope at an accelerating voltage of 80 kV and were used to measure the surface-averaged mean cluster diameters ( $\langle d \rangle$ ) of each sample using a minimum of 200 clusters and the equation:

$$\langle \mathbf{d} \rangle = \frac{\sum n_i d_i^3}{\sum n_i d_i^2} \tag{2}$$

where  $n_i$  is the number of particles with diameter  $d_i$ . Particle uniformity was quantified by calculating the dispersity index  $(D_A)^{2^4}$ 

$$D_{\rm A} = \frac{\sum n_i \sum (\pi d_i^{\ 2})^2 n_i}{\left(\sum \pi d_i^{\ 2} n_i\right)^2}$$
(3)

Unsupported clusters were prepared for microscopy as described in Section 2.2.  $SiO_2$ -supported clusters were placed onto holey-carbon Cu grids after suspending the samples in acetone.

2.6. Removal of Protecting Polymers and Assessment of Surface Accessibility by  $O_2$  Chemisorption Uptakes. 2.6.1. Removal of the Protecting Polymer via Treatment in  $H_2$  at Low Temperatures. SiO<sub>2</sub>-supported Pt clusters (1% wt., prepared as described in Sections 2.1.2 and 2.4) were treated in flowing  $H_2$  (Praxair 99.999%, 0.25 cm<sup>3</sup> s<sup>-1</sup> g<sup>-1</sup>) at 348 K for 1 h followed by treatment at 423 K for 1 h (0.033 K s<sup>-1</sup>). The sample was subsequently treated as described in Section 2.6.3 to measure  $O_2$  chemisorption uptakes.

2.6.2. Removal of the Protecting Polymer via Treatment in EtOH/H<sub>2</sub>O and H<sub>2</sub> at Low Temperatures. SiO<sub>2</sub>-supported Pt clusters (1% wt., prepared as described in Sections 2.1.2 and 2.4) were stirred (310 rpm) for 20 h in 50 cm<sup>3</sup> g<sup>-1</sup> of 1:1 by volume EtOH (Sigma-Aldrich, >99.5%) and deionized H<sub>2</sub>O (resistivity ~0.06  $\mu$ S cm<sup>-1</sup>) heated to 351 K. The solids were recovered by centrifugation (133 Hz, 0.6 ks) and maintained at 353 K in stagnant air overnight before being treated in flowing H<sub>2</sub> (Praxair 99.999%, 0.25 cm<sup>3</sup> s<sup>-1</sup> g<sup>-1</sup>) at 423 K (0.033 K s<sup>-1</sup>) for 1 h. The sample was subsequently treated as described in Section 2.6.3 to measure O<sub>2</sub> chemisorption uptakes.

2.6.3.  $O_2$  Chemisorption Uptakes. The chemically accessible surface atoms of SiO<sub>2</sub>-supported Pt clusters treated as described in Section 2.6.1 or 2.6.2 were titrated by the dissociative chemisorption of O<sub>2</sub>. O<sub>2</sub> uptakes consistent with TEM-derived surface-averaged mean diameters were considered definitive evidence for clean surfaces and full polymer removal. Au surfaces, which do not chemisorb O<sub>2</sub> effectively,<sup>25</sup> cannot be used to obtain an accurate measure of particle size. Consequently, monometallic Pt/SiO<sub>2</sub> samples, not AuPt/SiO<sub>2</sub> samples, were used in all polymer removal experiments.

A volumetric adsorption apparatus outfitted with a Baratron gauge and a turbomolecular pump (Pfeiffer Vacuum, <1 Pa dynamic vacuum) were used to measure chemisorption uptakes. SiO<sub>2</sub>-supported Pt clusters (1% wt., prepared as described in Sections 2.1.2 and 2.4) were treated as described in Sections 2.6.1 or 2.6.2 and subsequently evacuated for 1 h at 423 K before cooling to 298 K. Isotherms were measured between 0.013 and 101.3 kPa O<sub>2</sub> (Praxair, 99.999%) using an equilibration time of 0.24 ks. O<sub>2</sub> uptakes were estimated by extrapolation to zero O<sub>2</sub> pressure. Metal dispersions were calculated using an adsorption stoichiometry of one O atom per Pt surface atom.<sup>26</sup>

$$\langle d \rangle = \frac{C}{D}$$
 (4)

where  $\langle d \rangle$  is the mean diameter in nm, *D* is the dispersion, and *C* is a function of the metal identity (1.13 nm for Pt), calculated assuming a spherical geometry and using the density of the bulk metal.<sup>27,28</sup>

## 3. RESULTS AND DISCUSSION

**3.1. Transmission Electron Microscopy.** Cluster size distributions obtained from transmission electron micrographs were used to calculate surface-averaged mean diameters of Pt and AuPt samples  $(Au_{33}Pt_{67}, Au_{50}Pt_{50}, and Au_{67}Pt_{33};$  Figure 1) using eq 2 (Table 2). Mean cluster sizes increased

Table 2. Surface-Averaged Mean Particle Diameters, Expected AuPt Mean Diameters, Dispersity Indices, and Relative Standard Deviations

	Au content (% at.)				
	0	33	50	67	
TEM-derived surface-averaged diameter, $\langle d \rangle \pm STD$ $\times N^{-0.5}$ (nm, eq 2)	2.7 ± 0.03	3.3 ± 0.04	3.5 ± 0.05	4.3 ± 0.07	
expected diameter, $d_{AuPt}$ (nm, eq 5)		3.3	3.7	4.2	
dispersity index, $D_A$ (eq 3)	1.10	1.15	1.25	1.31	
relative standard deviation (%)	14.7	18.2	21.9	22.8	

monotonically with increasing Au content of each sample (3.3, 3.5, and 4.3 nm, respectively), consistent with the incorporation of Au atoms into the starting Pt seed clusters (2.7 nm). The mean AuPt diameters ( $\langle d_{AuPt} \rangle$ ) of samples with different nominal Au contents were accurately described by the equation:<sup>29</sup>

$$\langle d_{\rm AuPt} \rangle = \langle d_{\rm Pt} \rangle \left( 1 + \frac{V_{\rm Au}' N_{\rm Au}}{V_{\rm Pt}' N_{\rm Pt}} \right)^{1/3} \tag{5}$$

Here,  $\langle d_{\rm Pt} \rangle$  is the surface-averaged mean diameter of the initial Pt seed clusters,  $V'_{Au}$  and  $V'_{Pt}$  are the atomic volumes of Au and Pt in their bulk zerovalent state, and  $N_{\rm Au}$  and  $N_{\rm Pt}$  are the number of Au and Pt atoms in each sample. Eq 5 is derived on the basis of the premise that solvated Au cations are reduced and dispersed across all Pt clusters uniformly and do not nucleate heterogeneously on the surfaces of a few select seed clusters that grow at the expense of the majority or nucleate homogeneously in solution to form the large (~10-100 nm) broadly distributed clusters typical of monometallic Au particles prepared under similar conditions. Both heterogeneous and homogeneous nucleation of Au would result in a bimodal particle size distribution containing the initial Pt seed cluster distribution and larger Au-rich clusters; the presence of such large particles would skew surface-averaged diameters (eq 2) to values larger than those predicted by eq 5. The observed agreement between the values measured by TEM and those predicted by eq 5 (Table 2) is consistent with uniform Pt seed cluster growth via addition of Au.

A more rigorous assessment of size uniformity is the calculation of the dispersity index ( $D_A$ , eq 3), which we report in Table 2, together with the more commonly reported, but less precise, relative standard deviation (ratio of the mean to the standard deviation) of the cluster diameters.  $D_A$  values are near unity (<1.5), consistent with clusters of uniform size, as defined by IUPAC.<sup>24,30</sup> Relative standard deviations (14.7–22.8%) are typical of colloidal clusters prepared using NaBH<sub>4</sub> reductants and thiol-based protecting agents<sup>31,32</sup> but were obtained here without protecting agents or the use of reductants containing S and B heteroatoms, which irreversibly titrate the surface atoms required for the catalytic function intended for such clusters.

**3.2. UV–Visible Spectroscopy.** UV–visible spectra were used to probe the extent of Au–Pt mixing within clusters. UV–visible spectra of Au clusters (prepared by the procedures in Section 2.1.3) exhibit a localized surface plasmon resonance (LSPR) band at 500–700 nm (Figure 2) that is typical of



**Figure 2.** UV–visible absorption spectra of (a) Pt clusters (- - -), (b) bimetallic Au<sub>50</sub>Pt<sub>50</sub> clusters (-), (c) a physical mixture of Pt and Au clusters  $(- \cdot)$ , and (d) Au clusters  $(\cdot \cdot \cdot)$ .

nanosized Au clusters larger than 2 nm in diameter.<sup>33,34</sup> Pt clusters, in contrast, do not exhibit detectable LSPR features; however, such features are evident in physical mixtures of monometallic Pt and Au clusters (Figure 2). Undesired Au-rich clusters formed from the homogeneous or heterogeneous nucleation of Au during synthesis (Scheme 1,1) would therefore be detected from their UV–visible spectra, even when such clusters coexist with monometallic Pt particles.

Bimetallic Au<sub>50</sub>Pt<sub>50</sub> clusters (synthesized as described in Section 2.1.5) do not show a plasmon resonance, indicating that monometallic Au clusters and core–shell particles with Pt<sub>core</sub>–Au<sub>shell</sub> arrangements did not form.<sup>35</sup> The Pt-like UV–visible spectra of these AuPt clusters indicate that particle surfaces contain a significant number of Pt atoms, which would dampen the surface plasmon oscillations of Au atoms, a conclusion similar to that reached from the Pd-like spectrum of AuPd particles prepared from Pd seed clusters.<sup>12</sup> As proposed in the case of AuPd, the prevalence of seed cluster metal atoms (Pt or Pd) at bimetallic cluster surfaces suggests that Au cations replace surface Pt or Pd atoms via galvanic displacement reactions (Scheme 1,2a) and that they are subsequently covered by Pt or Pd atoms that return upon rereduction of their solvated cations by solvent molecules (Scheme 1,2b).

**3.3. Elemental Analysis of Individual Particles by EDS.** The uniformity of bimetallic mixing and its mechanistic implications are most accurately examined through particle-by-particle elemental analysis using EDS; such methods also allow us to confirm the exclusive presence of bimetallic clusters, as well as to rigorously assess how the size of the parent seed (Pt or Pd) relates to its ultimate Au content. The mean atomic fraction of Pt or Au in a bimetallic sample was calculated using data from more than 100 bimetallic particles and eq 1. Mean EDS-derived compositions agree with those predicted from the



Figure 3. Parity plots of the measured and expected mean Au content ( $\langle$ Au content $\rangle$ ) of (a) AuPt and (b) AuPd particles. Experimental atomic compositions were determined via particle-by-particle elemental analysis of over 100 particles per sample using EDS and eq 1.



**Figure 4.** Changes in mean Au content (from EDS data) with (a) AuPt particle diameter  $d_{AuPt}$  (from HAADF imaging) and (b)  $d_{AuPd}$ . Greater than 100 particles analyzed for each bimetallic sample. Samples with nominal Au contents of 33% at. ( $\blacklozenge$ ), 50% at. ( $\blacksquare$ ), and 67% at. ( $\bigstar$ ) shown. Particles binned by particle diameter (bin width of 0.5 nm), with bins containing less than 3 particles omitted for clarity and 74–87% of particles located within 4 bins.

reagent mixtures used (Figure 3a), thus confirming the full recovery of metals and of their cationic precursors as part of the colloidal particles. Data obtained via EDS analysis of AuPd clusters are also included in Figure 3; they similarly show that the expected compositions were achieved. No monometallic clusters were detected in any of the AuPt or AuPd bimetallic samples.

Next, we examine how the chemical composition of individual particles changes with cluster size to assess the compositional uniformity of each sample and to infer the synthesis routes by which they form. Au content (% at.) increased with increasing cluster size (Figure 4a), indicating that larger AuPt particles within a given AuPt sample contain relatively more Au atoms than smaller ones. Such Au enrichment in larger particles becomes more evident in samples with higher mean Au fractions. As a result, the omission of a few undetected particles with high Au compositions in the calculation of the mean atomic fraction of Au (eq 1) for such samples would lead to underestimates of Au content; this appears to be the case for the Au<sub>67</sub>Pt<sub>33</sub> sample, for which the EDS-derived % at. Au content falls below the parity line shown in Figure 3a.

In contrast with the trends observed for AuPt clusters, the Au content (% at.) of individual AuPd clusters decreased with increasing cluster size (Figure 4b).  $M_B$  seed clusters grow via the addition of Au atoms; thus, dissimilar trends in the effects of cluster size on bimetallic composition for AuPd and AuPt systems suggest, in turn, dissimilar growth mechanisms, consistent with the different synthetic protocols required to achieve size and compositional uniformity in AuPd and AuPt samples (discussed later in Section 3.4).

Next, we derive the equations that govern cluster growth via GDR to determine the relevant parameters that influence the amount of Au added to each parent seed cluster and their sensitivity to cluster size. The mechanistic features of GDR, the proposed growth mechanism for AuPd clusters,<sup>12</sup> are below:

- (a) Seed particle surface atoms ( $M_A$  = Pt or Pd) act as reductants for solvated cations of the more noble metal species ( $M_B$  = Au; Scheme 1,2a).
- (b) Oxidized seed atoms brought into solution by step (a) are subsequently reduced by the solvent and return to the surface of the growing bimetallic clusters (Scheme 1,2b).
- (c) Atoms of M<sub>A</sub> are replenished at the cluster surface in step
   (b) and thus continue to serve as reductants of solvated M<sub>B</sub> cations.

Such growth pathways require that solvated  $M_B$  cations encounter, and are therefore reduced by,  $M_A$  atoms instead of encountering  $M_B$  atoms at cluster surfaces. The growth rate of a spherical particle, *i*, is therefore proportional to its surface area  $(A_i)$ , as expressed by

$$\frac{\mathrm{d}N_i}{\mathrm{d}t} = A_i k \tag{6}$$

where  $N_i$  is the moles of atoms in a growing cluster and k is the areal rate constant for the galvanic displacement reaction.  $N_i$  and  $A_i$  in eq 6 were expressed as functions of the cluster diameter,  $d_i$ , and the resulting differential equation was solved to give the thickness by which each seed cluster grows ( $\Delta d_i$ ) as a result of the addition of Au atoms (derivation in Section S1):

$$\Delta d_i = 2V'_i kt \tag{7}$$

Here,  $V'_i$  is the atomic volume of the particle and *t* is time. Eq 7 shows that the diameter of each parent seed cluster increases by a value ( $\Delta d_i$ ) that does not depend on the size of the initial seed cluster.<sup>12,36,37</sup> Consequently, seed particles with distributed diameters that all grow by the same amount ( $\Delta d$ ) via addition of Au atoms lead, in turn, to AuM<sub>A</sub> clusters with distributed compositions; larger seed particles give rise to bimetallic clusters with lower Au fractions (Scheme 3), as shown by rearranging eq 5 for an individual cluster, *i*:

$$\left(\frac{N_{\rm Au}}{N_{\rm M_A}}\right)_{\rm i} = \left[\left(1 + \frac{\Delta d}{d_{\rm M_A,i}}\right)^3 - 1\right] \frac{V_{\rm M_A}'}{V_{\rm Au}'} \tag{8}$$

Scheme 3. Inverse Dependence of % at. Au content on Particle Size for Bimetallic Particles Formed via GDR Processes





$$d_{\mathrm{AuM}_{\mathrm{A}},i} = d_{\mathrm{M}_{\mathrm{A}},i} + \Delta d \tag{9}$$

The expected inverse dependence of Au % at. on particle size was evident for AuPd but not for AuPt particles (Figure 4),

suggesting that Pt seed clusters grow by a thickness  $(\Delta d)$  that depends on the parent seed cluster diameter; thus, the requirements for GDR (a-c) stated above may not be fully met for AuPt compositions, and additional Au cation reduction routes may contribute to cluster growth during the synthesis of AuPt clusters.

The dependence of  $\Delta d$  on the initial Pt or Pd seed size was determined using particle-by-particle EDS elemental analysis and HAADF imaging to measure the atomic fraction of  $M_A$  $(X_{MA,i})$  and the particle diameter  $(d_{AuMA,i})$ , respectively, of each bimetallic cluster, *i*. These data were used to calculate the number of Pd or Pt atoms within each bimetallic cluster and, accordingly, the diameter of the parent Pd or Pt seed cluster from which each bimetallic cluster, *i*, was formed (derivation in Section S2). Seed cluster diameters were subtracted from  $d_{AuMA,i}$  to determine the thickness by which each Pd or Pt seed grows  $(\Delta d_i)$  via the addition of Au atoms:

$$\Delta d_{i} = d_{\text{AuM}_{\text{A}},i} \left[ 1 - \left( \frac{x_{\text{M}_{\text{A}},i} V'_{\text{M}_{\text{A}}}}{x_{\text{M}_{\text{A}},i} V'_{\text{M}_{\text{A}}} + x_{\text{Au},i} V'_{\text{Au}}} \right)^{1/3} \right]$$
(10)

Here,  $V'_{MA}$  and  $V'_{Au}$  are the atomic volumes of  $M_A$  and Au. Eq 10 is valid when  $M_A$  surface atoms removed via oxidation and dissolution from cluster surfaces (Scheme 1,2a) return to cluster surfaces at rates that are strictly proportional to their respective surface areas (requirement (b); Scheme 1,2b). In such cases, the number of  $M_A$  atoms removed equals the number returned to each cluster, thus rendering them available for galvanic displacement when solvated Au ions again reach those surfaces (requirement (c); Scheme 1,2a).

Figure 5 shows the effects of seed cluster size on  $\Delta d$  values for different nominal AuPd and AuPt compositions. The  $\Delta d$ values of AuPd clusters did not vary monotonically with seed size (Figure 5b), thus exhibiting the behavior expected for GDR processes, for which deposition and rereduction rates are both proportional to surface area and Au cations arriving at cluster surfaces find Pd surface atoms (instead of Au atoms) with a probability that is independent of seed cluster size. The expected  $\Delta d$  values for each composition can be calculated using the TEM-derived size distribution of the initial seed particles and distributing Au atoms among them based on particle surface area (derivation in Section S3).<sup>12</sup> The calculated  $\Delta d$  values for the AuPd samples agree well with EDS-derived values (Figure 5b; dashed line indicates calculated  $\Delta d$  values), consistent with GDR processes during synthesis.

In contrast with Pd clusters,  $\Delta d$  values increased as the Pt seed clusters became larger (Figure 5a), suggesting that Au atoms deposit on larger Pt seeds more frequently than predicted from their surface areas alone. Au and Pt, unlike Au and Pd, are immiscible within large bulk crystals ( $\Delta H_{AuPt} = +2.3 \text{ kJ mol}^{-1} \text{ vs } \Delta H_{AuPd} = -6.7 \text{ kJ mol}^{-1}$ ),<sup>16,17</sup> thus exhibiting a greater tendency for intracluster segregation, which would preferentially place Au atoms, with their lower surface energies,<sup>18</sup> at bimetallic surfaces. Au surface segregation becomes more evident for larger particles because their larger bulk reservoirs mitigate the depletion of Au from the bulk upon segregation, thus maintaining the thermodynamic driving force for Au surface enrichment.<sup>22</sup>

As Au atoms diffuse to the cluster surface, Pt surface coverage decreases, thus increasing the probability that solvated Au cations will encounter surface  $Au^0$  atoms instead of the Pt<sup>0</sup> atoms required for GDR. Consequently, the reduction of Au

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**Figure 5.** Effects of initial seed cluster diameter  $(d_{MA})$  on the growth  $(\Delta d)$  of (a) Pt and (b) Pd seeds. Horizontal dashed lines in (b) denote expected  $\Delta d$  values assuming GDR growth, calculated from TEM-derived Pd seed particle size distributions. At least 100 particles analyzed for each bimetallic sample using EDS and HAADF imaging. Samples with nominal Au contents of 33% at. ( $\blacklozenge$ ), 50% at. ( $\blacksquare$ ), and 67% at. ( $\blacktriangle$ ) shown. Particles binned by initial seed particle diameter (bin width of 0.5 nm), with bins containing less than 3 particles omitted for clarity and 90–95% of particles located within 4 bins.





<sup>*a*</sup>(a) Parent Pd clusters grow by a value  $\Delta d$  that is independent of seed cluster size, confirming that solvated Au cations encounter Pd<sup>0</sup>, not Au<sup>0</sup>, atoms at the growing bimetallic surface, and that GDR processes predominate during AuPd synthesis. (b) In contrast, parent Pt clusters grow by a value  $\Delta d$  commensurate with their size, consistent with higher Au<sup>0</sup> concentrations at the surface of the larger bimetallic clusters that lead to the fast, autocatalytic reduction of Au cations and the scavenging of solvated Au cations away from smaller clusters.<sup>22,23</sup>

cations by Pt<sup>0</sup> via galvanic displacement is hindered, and autocatalytic reduction by ethylene glycol on Au<sup>0</sup> sites becomes the predominant reduction route (Scheme 4). Autocatalytic reduction processes are fast,<sup>22,23</sup> as shown by the formation of large Au clusters in the absence of Pt seeds. Larger AuPt particles with higher Au<sup>0</sup> surface contents quickly scavenge Au cations via autocatalytic routes, leading such larger particles to acquire an amount of Au no longer in proportion to their respective surface areas, with  $\Delta d$  values larger than for smaller clusters (Figure 5a). Such phenomena become apparent for AuPt, but are not detectable for AuPd, because endothermic alloys exhibit a much greater preference for Au surface segregation than their exothermic counterparts, thus generating significantly more autocatalytic reduction sites than AuPd clusters. Such sites coexist with Pt<sup>0</sup> surface atoms, as confirmed by the Pt-like UV-visible spectra of AuPt clusters (Figure 2), that reduce Au cations via GDR routes and mitigate the autocatalytic reduction processes that, on their own, would lead to the large nonuniform clusters typical of monometallic Au.

**3.4.** Synthetic Protocols to Enhance Compositional Uniformity of AuPt Bimetallic Clusters. The protocols developed for AuPd clusters (Section 2.1.4; with EG instead of

EtOH/H<sub>2</sub>O as solvent) led to a bimodal distribution of AuPt cluster sizes (Figure S1 in Section S4), with one component identical in size and shape to that of the initial Pt seed clusters and another consisting of much larger clusters ( $\sim$ 5–20 nm). These larger clusters contain a disproportionate fraction of the Au atoms, thus compromising the size and compositional uniformity of the bimetallic materials. Next, we discuss the synthetic protocols that we have developed in order to synthesize more uniform AuPt clusters, and which were used to synthesize the bimetallic AuPt clusters discussed in detail in the preceding sections.

In addition to the enrichment of Au at the AuPt cluster surface (resulting from the immiscibility of Au and Pt; discussed in the preceding section), several other hurdles inherent to the AuPt system render the synthesis of uniform AuPt clusters more challenging than AuPd. The galvanic displacement of seed atoms by Au precursors is the sole kinetically relevant step of GDR;<sup>12</sup> however, the thermodynamic driving force for galvanic displacement of Pt<sup>0</sup> by Au cations is lower than for the corresponding Pd<sup>0</sup> reaction in the AuPd system (Scheme 1,2a;  $\Delta E_{redox,AuPt}^{\circ} = 0.34$  V,  $\Delta E_{redox,AuPd}^{\circ} = 0.53$  V; Table 1). In addition, a stronger reductant (EG instead of



**Figure 6.** UV-visible spectra of  $Au^{3+}$  in EG heated to 423 K in (a) the absence of Pt clusters and (b) the presence of Pt clusters (50% at. Pt). The intensity of the  $Au^{3+}$  precursor band at 323 nm ( $\blacklozenge$ ) decreased to negligible values (stage I), at which point the Au species nucleated (\*) and a LSPR band emerged at 530 nm (gray  $\blacksquare$ , stage II). Absorbance in the background region of the spectra at 410 nm ( $\triangle$ ) in stage I was negligible and constant in the absence of Pt clusters (a) but increased steadily in the presence of Pt clusters (b).

![](_page_8_Figure_3.jpeg)

Figure 7. Particle size distributions of  $Au_{50}Pt_{50}$  cluster suspensions, synthesized with (a) EG or (b) BD as the reductive solvent. The Au precursor solution was added all at once to a suspension of the preformed Pt seed particles heated to 423 K.

EtOH used for AuPd;  $E_{EG}^{\circ} = -0.8 \text{ V}$ ,  $E_{EtOH}^{\circ} = -0.197 \text{ V}$ ) was required to stabilize Pt seed clusters (as discussed in Section 2.1.2). The less favorable GDR thermodynamics for AuPt leads to slower displacement processes at cluster surfaces relative to AuPd, while the stronger reductant competes with Pt<sup>0</sup> surface atoms in reducing solvated Au cations. These kinetic and thermodynamic hurdles conspire to increase nonuniformity by decreasing the contributions of GDR routes to cluster growth relative to those from autocatalytic reduction processes and relative to the creation of pure Au nuclei in solution (homogeneous nucleation) or on the surfaces of preformed seed clusters (heterogeneous nucleation); these small Au structures then quickly grow into Au-rich clusters without the intervention of Pt<sup>0</sup> atoms as reductants.

UV-visible spectroscopy was used to examine Au atom deposition dynamics and the role of Pt seeds in scavenging Au cations in order to design synthetic protocols that would favor GDR processes over competing reduction routes. UV-visible spectra (Section 2.3) were used to monitor changes in the concentration of solvated Au<sup>3+</sup> precursors (323 nm)<sup>22</sup> and to

detect the incipient formation of Au-rich surfaces on clusters  $(530 \text{ nm}; \text{LSPR band})^{35}$  during the reduction of Au cations at 423 K in EG, with and without the presence of Pt seed clusters.

Au<sup>3+</sup> cations were reduced to concentrations below detection limits in <0.3 ks when Pt seed clusters were not present (Figure 6a). The Au<sup>0</sup> LSPR band, characteristic of the nucleation and growth of Au clusters, emerged only after the Au<sup>3+</sup> spectral features disappeared. The reduction of Au<sup>3+</sup> cations without the concomitant formation of Au clusters indicates that Au<sup>3+</sup> reduced to Au<sup>+</sup>, which absorbs at photon energies below 200 nm<sup>38</sup> (an inaccessible spectral range in these studies), or to Au<sup>0</sup>. The background absorbance in spectral regions without Au<sup>3+</sup> bands or LSPR features (i.e., 410 nm) was negligible in the absence of nanoparticles but became more intense after Au nucleation as a result of an increase in the particle mass in the suspension, which became darker and redder after nucleation. The overall reaction appears to involve the sequential reduction of  $Au^{3+}$  precursors (stage I) and the growth of Au clusters (stage II), mediated by the intervening formation of nuclei (Figure 6a).

Au<sup>3+</sup> cations added to a suspension of Pt clusters and treated similarly to the seed-free solution were reduced fully in <0.3 ks (stage I) before the detection of the Au<sup>0</sup> LSPR band characteristic of the nucleation and growth of Au-rich clusters (stage II; Figure 6b). The background absorbance was evident at the beginning of stage I because Pt seed clusters were present. This background absorbance subsequently increased monotonically with time, without the concomitant emergence of detectable LSPR bands, in contrast to the negligible and invariant background evident during Au3+ reduction in the absence of Pt seeds (stage I, Figure 6a). This increase in background absorbance is indicative of an increase in particle mass, which taken together with the absence of LSPR features in stage I, suggests that seed clusters grow without evidence for the formation of monometallic Au surfaces. Transmission electron micrographs of the clusters formed indicate that the size distribution shifted uniformly to clusters larger than the Pt seeds (Figure 7a), consistent with the uniform placement of Au atoms across all Pt clusters in stage I. Larger clusters (~5-10 nm), absent in the parent seed distribution, were also evident in these micrographs. These large clusters were Au-rich, and their formation reflects the inability of Pt<sup>0</sup> surface atoms to reduce all the solvated Au cations before they can form nuclei that grow via fast autocatalytic reduction routes. The formation of bimetallic particles of uniform size and composition thus requires that we extend stage I for longer periods of time in order to allow the uniform dispersion of all Au atoms onto the Pt seeds while preventing the nucleation and growth that leads to large Au-rich clusters (stage II). The discussion that follows aims to describe how various synthesis parameters can be adjusted to inhibit Au nucleation and promote GDR reduction by surface Pt<sup>0</sup> atoms.

3.4.1. Effects of Solvent Reduction Potential on the Formation of Bimetallic AuPt Clusters. The nucleation of Au-rich clusters may be prevented by the exclusion of all reductants, other than the Pt seeds, from synthesis mixtures, which would ensure that  $Pt^0$  surface atoms are the only reductant. The formation of the initial seed clusters and the reduction of Pt cations formed in galvanic displacement processes (Scheme 1,2b), however, require an additional reductant, which in this case, also acts as the solvent; this reductant competes with  $Pt^0$  atoms in the reduction of Au cations (Scheme 1,1). Here, we examine how the reduction potential of the solvent impacts the extent to which Au and Pt atoms combine to form bimetallic AuPt clusters.

The mean diameter of monometallic Pt clusters synthesized in butanediol (BD; 2.3 nm  $\pm 0.02$ ) is smaller and their size more narrowly distributed than Pt clusters prepared via similar protocols with EG (2.7 nm  $\pm 0.03$ ; Figure 7), consistent with the faster reduction of Pt cations by BD than EG and with the subsequent formation of more Pt nuclei that then grow into smaller and more narrowly distributed clusters;<sup>39</sup> thus, BD acts as a stronger reductant than EG. Next, we show that increasing the reductive strength of the solvent (from EG to BD) also decreases the growth of Pt seeds as bimetallic clusters uniform in composition and promotes instead the formation of large Au-rich clusters.

 $Au_{50}Pt_{50}$  suspensions were prepared by adding a  $Au^{3+}$  solution all at once to a suspension of Pt seed clusters and treating the resulting mixture at 423 K for 0.33 h. Figure 8 shows the LSPR intensity of the AuPt suspensions formed from these protocols with either EG or BD as solvents (deconvolution methods in Section 2.3). Samples formed with

![](_page_9_Figure_6.jpeg)

Figure 8. LSPR intensity of bimetallic  $Au_{50}Pt_{50}$  suspensions synthesized in EG (a, -) and BD (b, - -) at 423 K. The Au precursor solution was added all at once to a suspension of preformed Pt seed particles heated to 423 K.

BD gave more intense LSPR features than with EG, indicating that the stronger reductant favors the formation of monometallic Au surfaces. TEM-derived size distributions were bimodal for BD-derived samples, with one component identical in size and shape to that for the Pt seed clusters and another composed of much larger clusters (>5.5 nm; Figure 7b), apparently formed via nucleation and growth of Au-rich clusters. With EG as the solvent, a few large clusters also formed, but the predominant component consisted of clusters shifted in size from those of the Pt seeds (Figure 7a), consistent with the predominant deposition of Au atoms onto seed clusters.

These data show that stronger reductants increase the rate of nucleation and growth of Au-rich clusters (Scheme 1,1), thus precluding the reduction of Au cations by Pt<sup>0</sup> surface atoms via GDR processes (Scheme 1,2), a requirement for compositional uniformity. Weaker reductants favor GDR but must still be capable of stabilizing clusters and of reducing the cations formed from seed clusters in GDR processes in order to return the less noble metal to the bimetallic clusters (Scheme 1,2b).

3.4.2. Effects of the  $Au^{3+}$  Addition Rate on the Size and Compositional Uniformity of AuPt Clusters. Nucleation rates can be decreased by decreasing the concentration of the solute that forms the nuclei.<sup>40</sup> We show here that adding the Au precursor solution in a slow and precise manner using a syringe pump maintains a low concentration of Au species in solution and extends the regime of uniform Pt seed cluster growth (stage I; Figure 6) by delaying or even preventing nucleation of Au to form Au-rich clusters. The effects of the Au cation addition rate on the size and compositional uniformity of the resulting bimetallic  $Au_{50}Pt_{50}$  clusters were determined by adding EG solutions of Au precursors dropwise at varying rates to the starting Pt seed cluster suspensions (in the EG solvent) at 423 K.

LSPR bands were not detected when Au precursor solutions were added slowly ( $\leq 25 \text{ nmol Au}^{3+} \text{ s}^{-1}$ ) to Pt cluster suspensions; large clusters (>5.5 nm) were not detected by TEM in the clusters formed (Figure 9). The surface-averaged mean diameter (eq 2) of AuPt clusters prepared using a Au<sup>3+</sup> addition

![](_page_10_Figure_2.jpeg)

Figure 9. (a) Plasmon resonance intensity of bimetallic  $Au_{50}Pt_{50}$  clusters synthesized in EG with varying rates of addition of the Au precursor to a Pt cluster suspension heated to 423 K. (b) Particle size distribution of Pt seed clusters (gray) and bimetallic  $Au_{50}Pt_{50}$  clusters (black) prepared using a Au precursor addition rate of 16.7 nmol  $Au^{3+}$  s<sup>-1</sup>.

rate of 16.7 nmol Au<sup>3+</sup> s<sup>-1</sup> is consistent with the homogeneous distribution of Au atoms among seed clusters (eq 5; Table 2) and with EDS analysis of >100 clusters showing no Au-rich clusters (Figure 3a). Higher rates of addition of Au precursors (>25 nmol Au<sup>3+</sup> s<sup>-1</sup>) led to AuPt samples with significant LSPR bands (Figure 9a), consistent with the extensive formation of Au-rich clusters.

The slow addition of Au precursors minimizes the concentration of solvated Au species and precludes conditions that favor the abrupt creation of a large number of Au nuclei, typically denoted as a nucleation burst.<sup>41</sup> Au nuclei rapidly consume all solvated Au cations via deposition onto Au-rich clusters, thus preventing their incorporation into AuPt clusters. Slow Au<sup>3+</sup> addition rates therefore ensure that Pt<sup>0</sup> atoms present at bimetallic cluster surfaces, as confirmed by the Pt-like UV-visible spectra of AuPt clusters (Figure 2), are able to reduce Au cations via GDR processes while the Au<sup>0</sup> surface atoms also present at cluster surfaces reduce solvated Au cations via autocatalytic routes<sup>42</sup> (as discussed in Section 3.3), thus precluding the formation of Au nuclei. The slow dropwise addition of Au precursors is not required for AuPd systems, for which autocatalytic reduction pathways were not detectable (Section 3.3). Such systems were prepared with a weaker reductant as solvent, are less prone to segregate Au atoms to cluster surfaces because of their favorable mixing enthalpies, and have more favorable galvanic displacement thermodynamics  $(\Delta E^0_{redox})$  than AuPt.

The intensity of LSPR bands decreased monotonically with increasing Au<sup>3+</sup> addition rate when Au precursor solutions were added quickly (>25 nmol Au<sup>3+</sup> s<sup>-1</sup>; Figure 9a). Higher Au<sup>3+</sup> addition rates result in a larger fraction of Au atoms added to synthesis mixtures and in contact with Pt seeds during the critical period of bimetallic cluster growth (stage I, Figure 6), thus increasing the fraction of Au atoms incorporated as AuPt clusters before reaching conditions that result in a nucleation burst. Consequently, the fraction of Au species available for Au cluster growth (stage II, Figure 6) is smaller and leads to weaker LSPR bands in the UV–visible spectra of the resulting sample.

3.4.3. Effects of Synthesis Temperature on the Size and Compositional Uniformity of Bimetallic Clusters. Nucleation

rates increase with temperature,<sup>40</sup> suggesting that lower synthesis temperatures may promote the formation of bimetallic particles via GDR (stage I, Figure 6) by delaying the nucleation of Au clusters. GDR rates are also affected by temperature, however, rendering the effects of synthesis temperature on the size and compositional uniformity of bimetallic clusters difficult to establish without direct experimental evidence. Such effects were determined by synthesizing bimetallic  $Au_{50}Pt_{50}$  clusters at various temperatures (388–423 K; Au precursor solutions in EG added at 16.7 nmol Au<sup>3+</sup> s<sup>-1</sup> to Pt seed cluster suspensions in EG).

LSPR band intensities of AuPt suspensions prepared using these protocols decreased with increasing synthesis temperature (Figure 10a), indicating that lower temperatures favor the formation of monometallic Au surfaces, in spite of lower Au nucleation rates. Au-rich clusters that result from homogeneous or heterogeneous nucleation events are significantly larger in diameter (>5.5 nm) than the Pt clusters that grow uniformly via addition of Au, resulting in a bimodal size distribution (Figure 7a). Here, we isolate the uniform growth component of these distributions by calculating the mean cluster diameter while omitting clusters larger than 5.5 nm ( $\langle d'_{AuPt} \rangle$ ). The  $\langle d'_{AuPt} \rangle$ value of clusters prepared at 388 K remained the same as that of the parent Pt seeds (Figure 10b), indicative of the absence of bimetallic growth. Higher synthesis temperatures led to larger  $\langle d'_{AuPt} \rangle$  values. The surface-averaged mean diameter of AuPt clusters synthesized at 423 K agreed well with the expected diameter (eq 5), and no large Au-rich clusters were detected, consistent with the consumption of all Au species within AuPt clusters and the effective prevention of Au<sup>0</sup> nucleation.

These data indicate that elevated temperatures favor the bimetallic growth characteristic of GDR processes. The unfavorable mixing enthalpies of AuPt formation are compensated by entropies of mixing that influence Gibbs free energies more strongly at higher temperatures.<sup>16</sup> In contrast, exothermic alloys such as AuPd can be synthesized at ambient temperature with GDR as the predominant growth mechanism.<sup>12</sup>

3.4.4. Synthesis of AuPt Clusters with >50% at. Au Content. The synthesis of uniform AuPt suspensions with >50% at. Au requires additional synthetic strategies to prevent

Plasmon Resonance Intensity

380

400

420

Temperature (K)

![](_page_11_Figure_1.jpeg)

380

400

Temperature (K)

420

440

**Figure 10.** (a) Plasmon resonance intensity and (b) the surface-averaged mean particle diameter of clusters <5.5 nm in diameter ( $\langle d'_{AuPt} \rangle$ ) of bimetallic Au<sub>50</sub>Pt<sub>50</sub> samples prepared at various synthesis temperatures. Black horizontal solid lines in (b) denote the initial Pt seed diameter (bottom) and the expected AuPt diameter (using eq 5, top). Clusters prepared in EG by adding the Au precursor to a stirring, heated suspension of Pt seed clusters at a rate of 16.7 nmol Au<sup>3+</sup> s<sup>-1</sup>.

440

![](_page_11_Figure_3.jpeg)

Figure 11. Changes in (a) plasmon resonance intensity and (b) dispersity index ( $D_A$ , eq 3) of AuPt clusters with increasing Au content. Clusters prepared (in EG) by adding the Au precursor dropwise to a stirring suspension of Pt seed clusters heated to 423 K.

the formation of large Au-rich clusters. AuPt samples composed of  $\leq$ 50% at. Au were prepared by adding Au precursor solutions dropwise (16.7 nmol Au<sup>3+</sup> s<sup>-1</sup>) to Pt seed cluster suspensions at 423 K and adjusting the volumetric ratio of the Au precursor solutions (5 × 10<sup>-4</sup> M in EG) and the Pt cluster suspensions (5 × 10<sup>-4</sup> M in EG, Pt atom basis) used in order to reflect the desired atomic ratio; these materials exhibited no detectable LSPR features (Figure 11a). Using the same protocols to create samples with higher Au contents (>50% at.), however, led to materials with significant LSPR features (Table S1, Section S5) and broad cluster size distributions (Figure S2, Section S5); these data indicate the substantial presence of Au-rich clusters that form via homogeneous or heterogeneous nucleation of Au.

Previously, we showed that decreasing Au precursor addition rates (to  $\leq 25$  nmol Au<sup>3+</sup> s<sup>-1</sup>) minimized the concentration of solvated Au species, thus preventing the nucleation of Au during the synthesis of Au<sub>50</sub>Pt<sub>50</sub> clusters (Section 3.4.2). Next,

we show that the synthesis of bimetallic samples with higher Au contents requires a further decrease in the addition rate of Au precursors in order to accommodate the larger number of solvated Au cations required for such compositions without causing a nucleation burst. AuPt suspensions with >50% at. Au content were prepared by first synthesizing  $Au_{50}Pt_{50}$  bimetallic clusters (as described above) and subsequently adding the balance Au precursor solution at a slower rate (4.17 nmol Au<sup>3+</sup> s<sup>-1</sup>). The LSPR intensities of the resulting cluster suspensions rose monotonically with increasing Au content up to 76% at. Au (Figure 11a). Further reductions of Au<sup>3+</sup> addition rate did not influence the LSPR intensities of the resulting clusters (Table S1 in Section S5).

The stronger LSPR bands for suspensions with higher mean Au contents may be caused by either an increase in the atomic fraction of Au at bimetallic cluster surfaces or the formation of large Au-rich clusters that compromise size and compositional

![](_page_12_Figure_2.jpeg)

**Figure 12.** TEM-derived and chemisorption-derived mean particle diameters (eqs 2 and 4, respectively) of 1% wt. SiO<sub>2</sub>-supported Pt clusters treated in (a) flowing H<sub>2</sub> at 523 K for 1 h ( $\blacksquare$ ), 423 K for 1 h ( $\blacktriangle$ ), 348 K for 1 h followed by 423 K for 1 h ( $\blacklozenge$ ), and 348 K for 1 h ( $\blacklozenge$ ) and of clusters treated in (b) a stirring mixture of 1:1 by volume EtOH/H<sub>2</sub>O ( $\bigtriangleup$ ) or deionized H<sub>2</sub>O ( $\Box$ ) at 351 K for 20 h prior to treatment in flowing H<sub>2</sub> at 423 K for 1 h. Points on the parity line indicate polymer-free surfaces. The dashed horizontal line at 2.7 nm denotes the diameter of untreated Pt clusters (determined by TEM).

uniformity. A measure of size uniformity,  $D_A$  (eq 3), was used to identify bimetallic cluster suspensions containing large Au-rich clusters; samples with  $D_A$  values >1.5 are considered nonuniform in size<sup>23,31</sup> and are therefore nonuniform in composition as well. D<sub>A</sub> values near unity for AuPt suspensions with  $\leq$ 76% at. mean Au content (Figure 11b) indicate that such samples are uniform in size and therefore composition, and suggest that their monotonic rise in LSPR intensity with increasing Au composition reflects an increase in the number of Au atoms at their bimetallic surfaces. These conclusions are consistent with the elemental analysis of Au<sub>67</sub>Pt<sub>33</sub> clusters using EDS, which detected no monometallic Au clusters, and with previous conclusions of cluster surfaces becoming enriched in Au during synthesis (Section 3.3). The large  $D_A$  value (14.8) of the Au<sub>85</sub>Pt<sub>15</sub> cluster suspension indicates the presence of large Au-rich clusters that account for the strong LSPR band in this sample (Figure 11a), and suggests that the protocols employed here are ineffective at preventing the nucleation of Au<sup>0</sup> in mixtures with very high Au contents ( $\geq 85\%$  at. Au).

The slower rates of Au<sup>3+</sup> addition required for AuPt cluster suspensions composed of >50% at. Au reflect the increasing difficulty of synthesizing uniform AuPt clusters as the surface becomes Au-rich and favors autocatalytic reduction by Au<sup>0</sup> surface atoms over GDR processes that use Pt<sup>0</sup> surface atoms as reductants. The lower rates of Au precursor addition maintain a low concentration of Au species in the synthesis mixture, thus preventing the nucleation of Au<sup>0</sup> and the formation of large Au-rich particles. In contrast, the synthesis of uniform AuPd clusters with >50% at. Au content does not require slow addition of the Au precursors,<sup>12</sup> reflecting the greater ease of synthesizing bimetallic particles of miscible metals, which do not exhibit intracluster segregation in the time scale of these synthesis protocols and thus maintain higher surface coverages of the less noble metal that favor GDR.

3.5. Removal of Polyvinylpyrrolidone (PVP) Species from Cluster Surfaces. The preparation of heterogeneous catalysts from colloidal suspensions of polymer-protected particles requires that we disperse such clusters onto a support, separate the solvent, and subsequently remove the polymer from metal surfaces in order to expose the active sites required for catalysis. High temperature treatments in O<sub>2</sub> are typically used to remove polymers, but often lead to cross-linking and densification that ultimately result in site-blocking amorphous carbon.<sup>43–46</sup> In contrast, treating supported clusters in  $H_2$  at low temperatures displaces the surface-binding carbonyl of PVP, releasing it from the metal surface without causing polymer densification.<sup>44</sup> Here, we disperse clusters onto SiO<sub>2</sub>, remove the solvent via centrifugation (Section 2.4), and use a low-temperature (≤423 K) treatment in a reducing environment ( $H_2$  or 1:1 by volume EtOH/ $H_2O$ ) to clean metal surfaces. Treated clusters are considered clean and chemically accessible when the surfaces of the clusters detected by TEM can be accurately titrated by chemisorbed oxygen, a condition that is met when the TEM-derived surface-averaged mean particle diameter becomes equal to the chemisorption-derived mean particle diameter. Pt surface atoms, but not Au surface atoms, can be accurately probed by chemisorbed oxygen;<sup>25</sup> hence, monometallic Pt clusters, not bimetallic AuPt clusters, were used in all deprotection studies. Au atoms that do not chemisorb oxygen effectively also bind adsorbates such as PVP more weakly than Pt atoms.<sup>47</sup> Monometallic Pt clusters that bind PVP more strongly than AuPt clusters are therefore an appropriate material to probe polymer removal protocols for AuPt alloys.

3.5.1. Removal of PVP from Pt Cluster Surfaces with  $H_2$ . The chemisorption-derived diameter of 1% wt. SiO<sub>2</sub>-supported Pt clusters treated in flowing H<sub>2</sub> at 523 K (1 h; 0.033 K s<sup>-1</sup> ramp rate), a temperature much higher than that at which PVP incipiently cross-links (423 K) to form dense and refractory polymer networks,<sup>45</sup> was larger than the surface-averaged diameter from TEM (Figure 12a), an indication of surface blockage by polymeric residues. The surface-averaged mean cluster diameter increased after treatment in flowing H<sub>2</sub> at 523 K (from 2.7 ± 0.03 to 3.0 ± 0.03 nm; measured by TEM). In contrast, the chemisorption-derived mean diameter of clusters treated at a lower temperature (423 K for 1 h; 0.033 K s<sup>-1</sup>) in flowing H<sub>2</sub> was similar to its TEM-derived mean diameter, suggesting that H<sub>2</sub> can remove PVP from Pt surfaces by treatment at temperatures below those leading to polymer densification. Clusters treated at 423 K were slightly larger than untreated ones, possibly as a consequence of local exotherms during polymer removal, which may have led to some coalescence among vicinal clusters.

The treatment of Pt clusters at a lower temperature (348 K for 1 h; 0.033 K s<sup>-1</sup>) in flowing H<sub>2</sub> before a subsequent treatment at 423 K (1 h; 0.033 K s<sup>-1</sup>) led to clusters of similar size to untreated ones but whose surfaces were still free of synthetic debris (Figure 12a). The additional step at 348 K removes the polymer more slowly by prolonging treatment at lower temperatures, and removes a larger fraction of surface-bound PVP before reaching higher temperatures, thus mitigating the generation of local exotherms from PVP removal reactions that lead to particle agglomeration. The chemisorption-derived mean diameter of clusters treated only at 348 K (1 h; 0.033 K s<sup>-1</sup> ramp rate) was larger than the mean diameter calculated from TEM, indicative of polymeric residues or partial Pt reduction.

3.5.2. Removal of PVP from Cluster Surfaces with H<sub>2</sub> and Either EtOH/ $H_2O$  or  $H_2O$ . The versatility of these lowtemperature reductive polymer removal methods was assessed by modifying the reductant. SiO<sub>2</sub>-supported Pt clusters (1% wt.) were treated in a reductive solvent (1:1 by volume EtOH/H2O) maintained at 351 K for 20 h instead of the treatment in flowing H<sub>2</sub> at 348 K. Clusters were subsequently separated from the liquid by centrifugation, dried in ambient air overnight at 356 K, and treated at 423 K (1 h; 0.033 K s<sup>-1</sup> ramp rate) in flowing  $H_2$  before  $O_2$  uptake measurements. The chemisorption-derived and TEM-derived mean diameters of EtOH/H2O/H2-treated clusters were similar and equal to the mean particle size of untreated clusters (determined by TEM; Figure 12b), indicating that metal surfaces were clean and that treating clusters in EtOH/H2O effectively replaces the H2 treatment step at 348 K.

In contrast, identical protocols with deionized  $H_2O$  instead of EtOH/ $H_2O$  led to clusters similar to those treated only at 423 K in  $H_2$ . The particle diameters derived from TEM and chemisorption data lie along the parity line, indicative of clean surfaces, but both diameters were larger than the diameter of untreated clusters (determined by TEM; Figure 12b), a reflection of some particle agglomeration during treatment. Treating clusters in deionized  $H_2O$  failed to remove a significant amount of surface debris, thus leading to local exotherms that can cause particle growth during the subsequent treatment at 423 K in flowing  $H_2$  (as discussed in Section 3.5.1). These results indicate that EtOH is required to remove the polymer from cluster surfaces, either as a reductant, helping to break the metal–PVP bond, or as a better solvent than  $H_2O$  for PVP.<sup>48</sup>

# 4. CONCLUSIONS

AuPt clusters uniform in size and composition were synthesized by colloidal methods using reagents containing only C, H, O, and N. These clusters were dispersed onto  $SiO_2$  and deprotected at low temperatures in a reducing environment without particle coalescence. In doing so, we provide not only catalysts of significant practical interest but also ideal materials to study the rigorous mechanistic descriptions of the effects of metal mixing. GDR synthesis protocols previously developed for an enthalpically favorable alloy (AuPd) were modified for an enthalpically unfavorable alloy (AuPt) to promote the uniform growth of Pt seeds via addition of Au and prevent the formation of large Au-rich clusters. Weaker reductants as solvents, slow addition of the Au precursors, high synthesis temperatures, and low Au<sup>0</sup> surface compositions were found to promote a more uniform distribution of Au across the parent Pt clusters. We show that the segregation of immiscible metals leads to the enrichment of Au<sup>0</sup> atoms at cluster surfaces, thus impeding reduction by surface Pt<sup>0</sup> via GDR while promoting fast autocatalytic reduction by surface Au<sup>0</sup>. The insights developed here can be applied to synthesize uniform bimetallic catalysts of other metal systems of interest, including those composed of immiscible metals.

## ASSOCIATED CONTENT

## **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemma-ter.6b02346.

Derivations of equations to express  $\Delta d$ , transmission electron micrographs of attempted syntheses of AuPt materials, and the intensity of LSPR bands in the UV– visible spectra of AuPt materials (PDF)

#### AUTHOR INFORMATION

#### **Corresponding Author**

\*E-mail: iglesia@berkeley.edu.

#### Notes

The authors declare no competing financial interest.

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